Magnetic Behavior of Europium Silicates Using Nuclear Gamma Resonance Spectroscopy *

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Dedicated to Prof. Dr. H. Maier-Leibnitz on the occasion of his 60th birthday

The ferromagnetic transition temperature, the quadrupole interaction, the hyperfine magnetic field, and the isomer shift have been measured in Eu_2SiO_4 and Eu_3SiO_5 using the 21.6 keV nuclear gamma resonance in ^{151}Eu. The isomer shifts found (-0.6 mm/sec for Eu_2SiO_4 and $+0.1$ mm/sec for Eu_3SiO_5 against EuS) are less negative than the values typical for other ionic Eu^{2+} compounds. The magnetic hyperfine fields (280 kOe for Eu_2SiO_4 and 240 kOe for Eu_3SiO_5) are much lower than the Eu^{2+} free ion value. A brief qualitative discussion of these hyperfine parameters is given. A rough correlation between the isomer shift and the transition temperature for various divalent Eu compounds is indicated. The effect of trivalent Eu impurities on lowering the Curie temperature of the silicates is demonstrated.

1. Introduction

The silicates of europium have been investigated recently for their structural, optical, magnetic, and luminescent properties[1–4]. Amongst the known stable phases of the (EuO-SiO_2) system, the orthosilicate Eu_2SiO_4 and Eu_3SiO_5 exhibit ferromagnetic behavior inspite of being ionic transparent insulators[1]. They have thus stirred considerable interest. Nuclear gamma resonance (NGR) is a powerful tool to probe the microscopic behavior of magnetic materials. In particular the 21.6 keV resonance in ^{151}Eu has excellent characteristics for investigating both the magnetic and chemical nature of europium ions. In this contribution we report NGR measurements of the hyperfine parameters in these silicates over the temperature region from 77 K to 1.5 K. From this we deduce the ferromagnetic transition temperature, the low temperature hyperfine magnetic field, and the isomer shift. A brief qualitative discussion of the findings is given.

2. Crystal Structure

Both these silicates are structurally complex. Eu_2SiO_4 has either orthorhombic[2] or monoclinic[3] structure depending on the method of synthesis. However, in pure crystals only the monoclinic phase is stable[3] at temperatures below 165 °C. A small impurity of Eu^{3+} seems to stabilize the orthorhombic phase at room temperature, but nothing is known about the temperature region below 77 K where our measurements were performed. In either structure the Eu^{2+} ion experiences a hexacoordination of oxygen ions, each of which belongs to a different SiO_4 tetrahedron.

Eu_3SiO_5 belongs to the tetragonal system with space group I4c2. The Eu^{2+} ions have two site symmetries. While at both the sites the Eu^{2+} ions are surrounded by distorted oxygen octahedra; the nearest and next nearest oxygen distances differ slightly for the two sites.

3. Experimental

Conventional experimental techniques of NGR spectroscopy have been adopted in the present investigation. All measurements were performed in transmission geometry with a 50 mCi source of $^{151}Sm_2O_3$. The source was always kept at roughly the same temperature as the absorber. All samples investigated have been obtained from IBM-Laboratories where the compounds have been synthesized by solid-state reaction of EuO

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and SiO_2 in a hydrogen atmosphere[1]. The resulting crystals were crushed by us into fine powder and absorbers of about 5 − 10 mg/cm² thickness were formed by spreading the powder into a disc-shaped lucite container. This then was sealed in an inert and dry atmosphere.

The NGR spectra were analyzed on an IBM 360/75 computer using a least-squares fitting routine discussed earlier[5].

All isomer shifts are given with reference to a standard EuS absorber[6].

4. Results

The resonance spectra of both silicates at 77 K showed a strong absorption centered around − 0.5 mm/sec. This isomer shift (IS) is representative of a divalent europium ion[7]. The width of this absorption peak is broader than that obtained with an equally thick paramagnetic EuS absorber using the same source. Since the Eu^{2+} ions in both silicates have a low site symmetry, the observed broadening is considered to be due to quadrupole interactions. Unfortunately the ratio of the nuclear quadrupole moments of the ground state and the 21.6 keV excited state is such that pure quadrupole spectra are commonly unresolved for this resonance[5]. The computer analysis gives an interaction energy of $e^2qQ = -12$ mm/sec in Eu_2SiO_4. A somewhat larger value was obtained for Eu_3SiO_5. However, in this compound Eu^{2+} ions occupy two sites with different symmetries and one actually should fit two different quadrupole spectra to the experimental spectrum. In view of the poor resolution, this was not attempted and only the average value for e^2qQ was derived. The results are given in Table 1.

In addition to the Eu^{2+} absorption a weak resonance is found near + 13.3 mm/sec. This corresponds to a trivalent europium impurity present in these compounds. In accordance with Ref.[3] this is to be expected by the method of preparation used. Because of the large differences in the IS between Eu^{2+} and Eu^{3+} ions, the NGR of ^{151}Eu provides a unique non-destructive method to estimate the Eu^{3+} content in Eu^{2+} compounds. Assuming the Debye-Waller factor (which gives the strength of the reso-

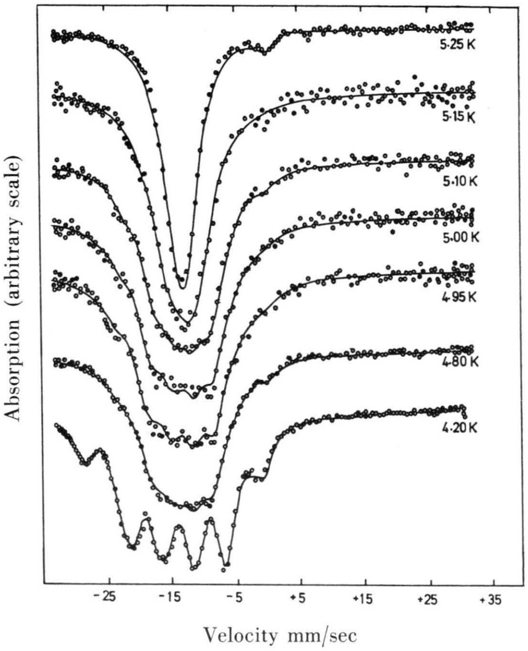

Fig. 1. NGR spectra of Eu_2SiO_4 at temperatures close to $T_c (= 5.2 \pm 0.5$ K). The solid lines are least squares fits as discussed in the text.

Table 1. Curie temperatures and hyperfine interaction parameters for Eu Silicates.

Compound	T_c (pure sample) K	T_c (our sample) K	Eu^{3+} (our sample) %	e^2qQ mm/sec	H_{hf} kOe	Isomer shift (vers. EuS) mm/sec
Eu_2SiO_4	9 [a]	5.2 ± 0.5	5	-12.0 ± 0.3 [c]	280 ± 5 [e]	-0.6 ± 0.1
Eu_3SiO_5	19 [b]	11.5 ± 0.5	8	-19.0 ± 10 [c, d]	240 ± 10 [e, d]	$+0.1 \pm 0.15$
Eu_3SiO_5						

[a] From Ref. [3]; [b] from Ref. [12]; [c] from spectrum taken at 77 K, [d] average value for both lattice sites; [e] from spectrum at 1.6 K.

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nance absorption) to be the same for both the impurity Eu^{3+} and the host Eu^{2+} ions, we have estimated the Eu^{3+} content in our samples. The results are also given in Table 1.

Both Eu_2SiO_4 and Eu_3SiO_5 are known to be ferromagnetic[1] at 4.2 K. The transition temperatures are reported[4] to be 7 K and 19 K, respectively. The NGR spectra measured well below the Curie temperature (T_c) showed a well developed hyperfine (hf) magnetic splitting. Close to the transition temperature the hf magnetic field (H_{hf}) decreases rather rapidly and becomes zero at T_c. In Fig. 1 we show spectra taken around T_c for Eu_2SiO_4. By plotting H_{hf} versus T and extrapolating for $H_{hf} = 0$, we find T_c to be (5.2 ± 0.5) K for Eu_2SiO_4 and (11.5 ± 0.5) K for Eu_3SiO_5.

Resonance spectra measured at 1.6 K were analyzed using a Hamiltonian for an axially symmetrie quadrupole interaction ($\eta = 0$) and with the direction of H_{hf} along the principal efg axis ($\Theta = 0$, $\Phi = 0$). Because of the low symmetry of the Eu^{2+} ions in the silicates these assumptions are surely an oversimplification. On the other hand, a fit with the correct Hamiltonian contains too many free variables and the fitting routine is unable to find a reproducible set of minimized parameters. Using a simulation program for the calculation of theoretical hf spectra we have shown earlier[5] that the structure of the spectrum is not sensitive to the chosen values of Θ and Φ, provided $g H_{hf} \gg e^2 q Q / 4 I (2I-1)$.

Furthermore, under this condition, the influence of η is barely noticable, in particular for values of $\eta < 0.4$. From these simulations it is seen that using the simple Hamiltonian described earlier, the deduced value of H_{hf} is correct within the experimental limits of error. But the number for $e^2 q Q$ returned by the fit is in general smaller than its actual value. This effect is clearly seen in our results, which give a value of $e^2 q Q = -4.3$ mm/sec from the fitting of the magnetic spectrum of Eu_2SiO_4. This number is about 30% of the value deduced from the pure quadrupole spectrum (Table 1). We take this as evidence that H_{hf} makes an angle with the principal efg axis. The spectrum of Eu_3SiO_5 did not show this effect quite so pronounced, but its analysis is further complicated by the presence of two lattice sites for Eu^{2+}. However, the spectra taken well below T_c clearly show that the magnetic hf fields must be nearly the same for both sites. The value for H_{hf} given in Table 1 is an average. From the observed line width we can set a limit of 10% for the difference in H_{hf} for the two sites. No difference in IS within the experimental errors was found for the resonances above and below the Curie points.

5. Discussion

The nature of the exchange interaction in divalent europium compounds has at present been discussed mainly for the chalcogenides[8]. The molecular field model is used in deriving the coupling between the nearest neighbors (J_1) and the next nearest neighbors (J_2). The relative strength of J_1 compared to J_2 determines the basic magnetic behavior since J_1 is a ferromagnetic coupling while J_2 is antiferromagnetic. A 4f-5d hybridization leads to an overlap of the orbitals of nearest neighbors and produces J_1. The antiferromagnetic coupling is due to superexchange via the p orbitals of the anions. Thus ferromagnetism ($J_1 \gg J_2$) is observed if the energy of promoting 4f electrons into 5d orbitals is small and if the 5d-4f overlap is large. The first condition is mainly governed by the lattice parameter, the second by the symmetry of the anion field. In the silicates the Eu^{2+} are surrounded by a distorted oxygen octahedron which presumably puts the t_{2g}-5d orbitals lower in energy than the e_g-5d orbitals. A simple minded comparision between the chalcogenides and the silicates thus predicts a rather high T_c for the latter[4]. However, the lowering of octahedral symmetry (distortion) will lift the degeneracy of t_{2g} orbitals, which in turn will reduce the 5d-4f overlap and thereby lower the transition temperature.

The electronic structure of the cation (Eu^{2+}) is reflected in the observed IS. From the above discussion it is obvious that there should be some relation between the IS, the transition temperature, and the type of ordering. We have plotted in Fig. 2 the IS of non-metallic compounds of Eu^{2+} versus the transition temperature as they are reported in the literature[9]. From this it can be seen that the Eu^{2+} compounds with higher transition temperature tend to show a higher s-electron density at the nucleus.

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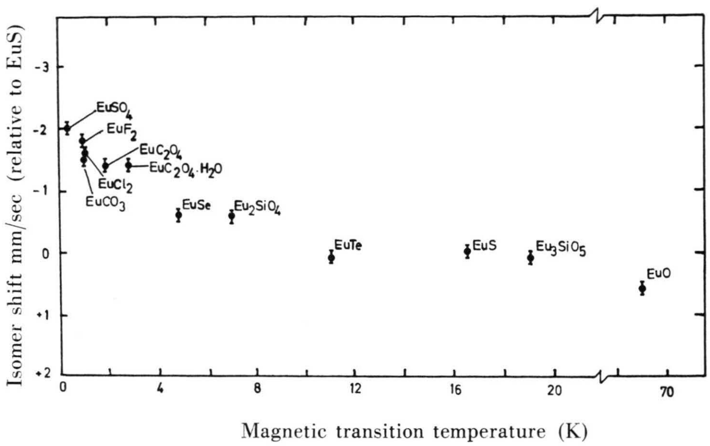

Fig. 2. Isomer shift of various non-metallic Eu^{2+} compounds plotted against their magnetic transition temperatures. Most of the data are taken from Ref. [9].

The antiferromagnetic ionic compounds like $EuSO_4$ are expected to come closest to a pure $4f^7$ configuration. The promotion of 4f electrons into 5d orbitals will increase the charge density at the nucleus, since the shielding of 6s electrons by 5d electrons is only about 30% of that by 4f electrons. Using a Hartree-Fock self-consistent field calculation [10] it should be posible to estimate the amount of 5d hybridization. However, we have refrained from doing so, because the effect of increasing 6s overlap with decreasing lattice parameter will also markedly influence the IS. Both these contributions are inseparable. The silicates in question show IS which are in general agreement with this qualitative picture. Although the silicates are usually termed "ionic compounds", it should be noted that their IS are less negative than the ones of the more typical ionic compounds (like $EuSO_4$ and EuF_2) and more in the region occupied by the chalcogenides. In addition, the hf fields found in both silicates are markedly lower than the value reported [11] for the free Eu^{2+} ion (−341 kOe). In contrast, the hyperfine fields of the ionic Eu^{2+} compounds ($EuSO_4$, EuF_2 etc.) are all rather close to the free ion number [9]. In the silicates an additional positive field, produced either by the dipolar contribution or by the 5d electrons, thus reduces the observed H_{hf}.

The values for T_c reported here are somewhat lower than those given by KALDIS et al. [3] and SHAFER [12]. This lowering of T_c can be attributed to the magnetic dilution of our samples by the non-magnetic Eu^{3+} ($^6F_0$) impurity ions. The estimated Eu^{3+} content of our samples is 5% in Eu_2SiO_4 and 8% in Eu_3SiO_5 (see Table 1). This finding is in agreement with an earlier report by MCGUIRE and SHAFER [13], who give $T_c = 4$ K for a sample of Eu_3SiO_5 containing roughly 20% Eu^{3+} impurities.

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